

A COMPARISON OF THE HYDRODESULFURIZATION AND HYDRODENITROGENATION ACTIVITIES
OF MONOLITH ALUMINA IMPREGNATED WITH Co AND Mo AND NALCOMO 474 CATALYSTS

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INTRODUCTION

In the wake of precarious supplies of petroleum, the need to turn to the abundant reserves of coal as an energy base can hardly be overemphasized. However, to accomplish the objective of using coal extensively, much research effort in the field of converting coal to environmentally clean and convenient fuel is required. The work presented here is so directed and is a part of the research program, at Oklahoma State University, which has the goal of tailoring catalysts for upgrading of liquids derived from coal.

In this study, a novel Monolith alumina structure was of interest as a base (or a carrier) material for Co-Mo-Alumina catalysts. The specific interest centered around assessing the suitability of the catalyst prepared by impregnating the novel alumina support with Co and Mo for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of a relatively high boiling stock. The Monolith catalyst was also tested on a low boiling coal-derived liquid.

OBJECTIVE

The objective of this work was to study the activity of the Monolith catalyst for removing sulfur and nitrogen from a Synthoil process liquid (heavy stock) and Raw Anthracene Oil (light feedstock), and to make a preliminary assessment of the advantages and/or disadvantages of the Monolith catalyst over a commercial catalyst used in the petroleum industry.

MATERIALS

Feedstocks:

As mentioned before, two coal-derived liquids were used. One was Raw Anthracene Oil obtained from Reilly Tar and Chemical Corporation. The other was a Synthoil liquid obtained from Pittsburgh Energy Research Center. The properties of these two liquids are given in Tables I and II. As is clear from the boiling point ranges of the two liquids, Synthoil is very high boiling as compared to the Raw Anthracene Oil.

Catalysts:

The properties of the two catalysts used in this study are given in Tables III and IV. The Monolith catalyst was prepared in the laboratory at OSU by impregnating Co and Mo on the Monolith alumina support received from the Corning Glass Company. The Nalco 474 catalyst was received from the Nalco Chemical Company. It is a commercial preparation and was used as a reference catalyst in this study.

Figure 1 shows the pore size distribution of the two catalysts as determined from the mercury porosimeter data. The most frequent pore radius of the Monolith catalyst is 80 \AA as compared to 33 \AA of the Nalco 474 catalyst. On the other hand, the surface area of the Monolith catalyst is 92.0 m²/gm. as compared to 240 m²/gm. of the Nalco 474 catalyst. The chemical compositions of the two catalysts also differ widely as shown in Tables III and IV.

TABLE I
PROPERTIES OF THE RAW ANTHRACENE OIL

	<u>Wt. %</u>
Carbon	90.3
Hydrogen	5.57
Sulfur	0.47
Nitrogen	1.035
Oxygen	2.625
Ash	Nil
API Gravity	-7

	<u>Boiling Range</u>	
<u>Volume Distilled,</u>	<u>Vapor Temperature, C(F),</u>	<u>Vapor Temperature, C(F),</u>
<u>Percent</u>	<u>at 50 mm Hg.</u>	<u>at 760 mm Hg.</u>
10	138.9 (282)	229.4 (445)
20	169.4 (337)	263.9 (507)
30	186 (367)	283.3 (542)
40	202.7 (397)	302.2 (576)
50	215 (419)	315.5 (600)
60	227.2 (441)	331.1 (628)
70	240.5 (465)	345 (653)
80	256 (493)	362.7 (685)
90	278.9 (534)	387.8 (730)

TABLE II
PROPERTIES OF THE SYNTHOIL LIQUID

	<u>Wt. %</u>
Carbon	80.5
Hydrogen	7.72
Sulfur	1.02
Nitrogen	1.19
Ash	3.4
Specific Gravity	1.12

Boiling Range		
<u>Volume Percent</u> <u>Distilled</u>	<u>Vapor Temperature, C(F),</u> <u>at 50 mm Hg.</u>	<u>Weight</u> <u>Percent S.</u>
10	170.5 (339)	0.2
20	211.6 (413)	0.242
30	260 (500)	0.332
33	276.6 (530)	0.366
Bottoms		1.7

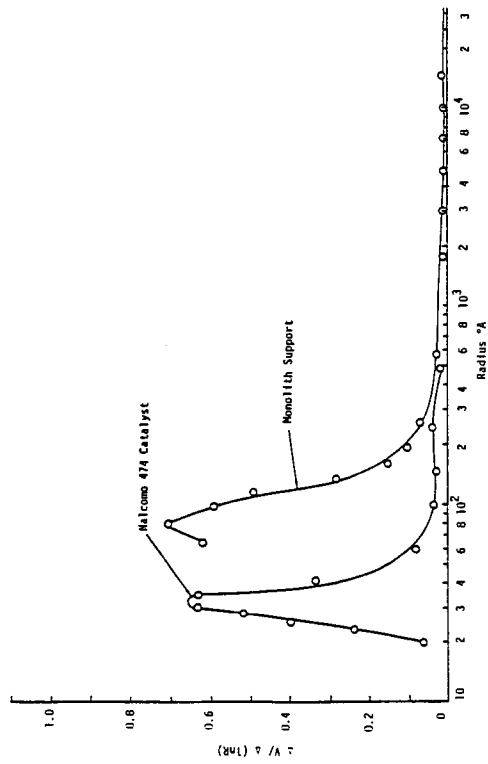
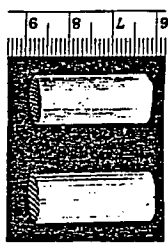
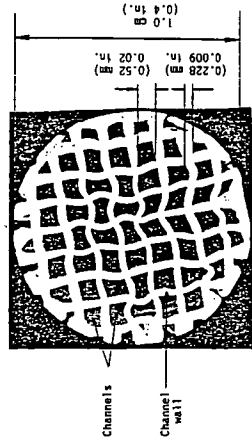


Figure 1: Pure Size Distribution of the Catalysts



Monolith Alumina Segments



Cross Section of a Monolith Alumina Segment

Figure 2: Monolith Alumina Structure

TABLE III
PROPERTIES OF THE MONOLITH CATALYST

	Wt. %
CoO	3.37
MoO ₃	7.25
Support	Alumina
Surface Area, m ² /gm.	92.0
Pore Volume, cm ³ /gm.	0.55
Most Frequent Pore Radius, °A	80.0

TABLE IV
PROPERTIES OF THE NALCOMO 474 CATALYST

	Wt. %
Alumina	82.39
MoO ₃	12.5
CoO	3.5
Na ₂ O	0.08
Fe	0.03
SiO ₂	1.5
Surface Area, m ² /gm.	240.0
Pore Volume, cm ³ /gm.	0.46
Most Frequent Pore Radius, °A	33.0

Figure 2 shows the shape and size of the Monolith alumina supports. These are in the form of cylindrical segments of about 2.54 cm. (1 in.) in length and about 1.0 cm. (0.4 in.) in diameter. These have longitudinal and parallel channels along their length. The size, shape and thickness of the walls of the channels are also shown in Figure 2.

The Monolith structure has about 60 to 80 percent of its cross-sectional area open. Therefore, a bed of regularly stacked Monoliths would offer significantly less pressure drop than that encountered in conventional packed beds. This has been observed by Satterfield and Ozel (1) for water-air systems. Some of the other important advantages listed by them are:

- (1) Where intraparticle diffusion appreciably affects the rate of the reaction, reduction in catalyst particle size would be necessary to increase the effectiveness factor and hence conversion. But this may not be possible due to the pressure drop limitations in conventional packed beds. In such situations, the use of Monoliths would provide the advantage of higher effectiveness factor.
- (2) When processing coal derived liquids which contain fine solid particles, the possibility of bed plugging may be minimized.
- (3) The flow of the liquid through regular channels would provide better gas-liquid contact, liquid distribution and wetting of the catalyst.

- (4) The compressive strength of Monoliths would be much higher than the catalyst particles generally used in packed beds. Therefore, the use of Monoliths would enable deep beds to be constructed without using intermediate supports and gas-liquid distributors.

All of the above advantages stem from the special geometry of the Monoliths as compared to that of the usual catalyst particles.

EXPERIMENTAL SETUP AND PROCEDURE

Reactor System:

A trickle bed reactor system was employed in this study. A schematic diagram of the experimental system is shown in Figure 3. The reactor was a 12.7 mm (0.5 in.) O.D. stainless steel tube packed with the catalyst. The catalyst bed height was 35.5 cms. (14 in.). When using Monolith catalyst, redistributors were put at intervals of 10.15 cms. (4 in.) each to ensure that the liquid passes through the channels. Figure 4 shows cross-section of the reactor packed with the Monolith and Nalcomo 474 catalysts. The latter catalyst was used in the form of 8-10 mesh (2 mm.) size particles.

The reactor was heated with the help of massive aluminum blocks placed around the reactor. The reactor temperature was measured at every inch of the catalyst height by traversing a thermocouple in a thermowell placed along the reactor bed. The reactor was operated at nearly isothermal conditions.

Method of Operation:

After loading the reactor with the catalyst and installing it in the experimental setup, the catalyst was activated. This was done by first calcining the catalyst at 232.2 C (450 F) and then sulfiding it with a mixture of 5.14 volume percent H_2S in H_2 . The reactor was then brought to the operating conditions and the flow of hydrogen and oil started. After about 32 hours of reactor-in-oil operation, representative product oil samples were taken at specified reactor conditions. The line out time of 32 hours was allowed to stabilize the activity of the catalyst. The product oil samples were analyzed for their sulfur and nitrogen contents with the help of a Leco Model 634-700 automatic sulfur analyzer and Perkin Elmes Model 240 elemental analyzer, respectively.

RESULTS

Figure 5 and 6 show the results of this study along with the results of Sooter (2) and Satchell (3) who conducted similar studies using the same experimental setup but with Nalcomo 474 catalyst and Raw Anthracene Oil. The graphs presented here are either weight percent sulfur or nitrogen in the product oil from the reactor vs. the volume hourly space time. Low sulfur or nitrogen in the product oil would correspond to higher activity of the catalyst under consideration.

The results with each feedstock and catalyst were obtained over a single reactor run lasting 105-132 hours. In each reactor experimental run, the start up reactor conditions were repeated at the end to check for loss, if any, of the catalyst activity. No significant decrease in catalyst activity was observed over the conditions studied.

The overall reproducibility of each reactor experimental run was checked by comparing the mode of response of desulfurization and denitrogenation to changes in space time as observed from the two reactor runs on the same feedstock. Figures 5 and 6 show that reactor runs were reproducible.

An estimate of the precision of sulfur and nitrogen analyses was made by analyzing Raw Anthracene Oil and Synthoil liquid a number of times. The results of sulfur

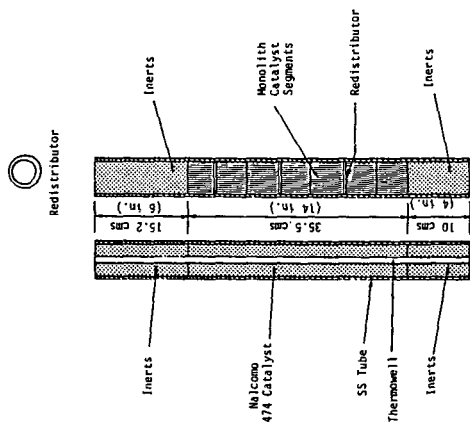


Figure 4: Cross Sections of the Reactors Packed with Nalco 474 and Monolith Catalysts

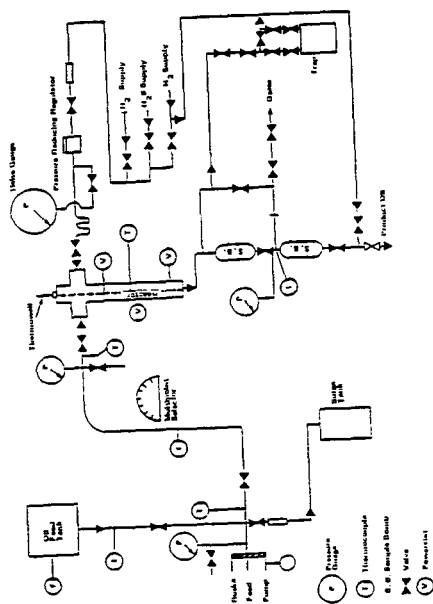


Figure 3: Reactor System

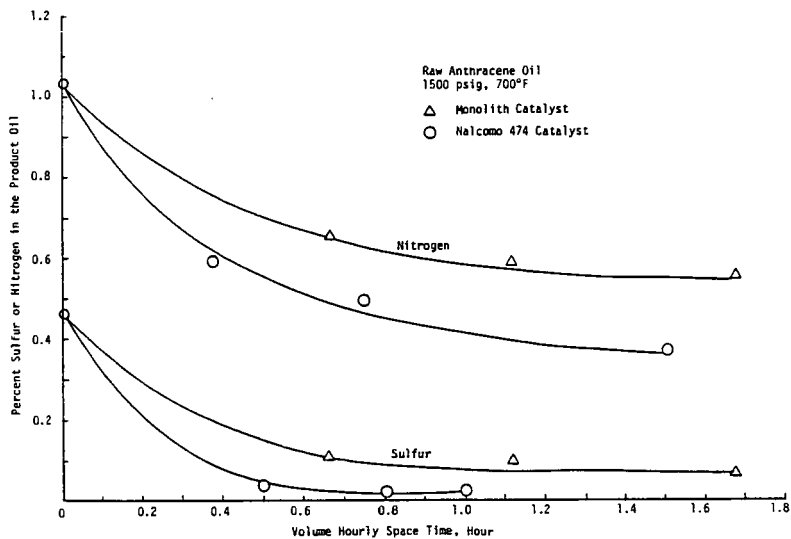


Figure 5: HDS and HDN Responses to the Changes in the Volume Hourly Space Time

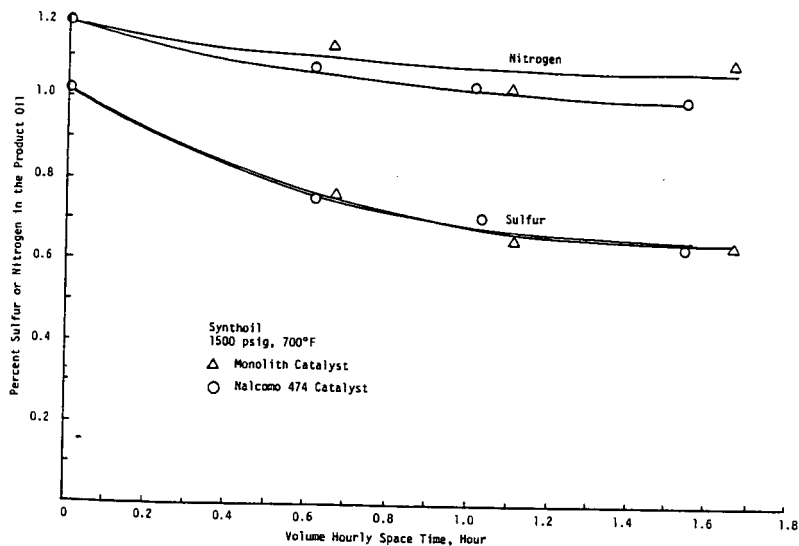


Figure 6: HDS and HDN Responses to the Change in the Volume Hourly Space Time

analysis of Raw Anthracene Oil were found to be precise within 0.25%. But precision of other results was within 5.0%.

DISCUSSION

Figure 5 indicates that on volume basis, the activity of the Monolith catalyst is less than the activity of Nalcomo 474 catalyst when Raw Anthracene Oil was the feed-stock. Similar behavior was observed when comparison was made on weight basis. Figure 6 shows that when tested on Synthoil, the HDS activity of the two catalysts were almost the same on volume basis. However, when comparison was made on the weight basis, Monolith catalyst was observed to remove more sulfur per unit weight of the catalyst.

Since the surface areas of the two catalysts differed widely, comparison of activities of the two catalysts on unit surface area basis was studied. Figures 7 and 8 represent such a comparison. The abscissa of these graphs is S/Q , where S is the total surface area of the catalyst in the reactor and Q is the volumetric flow rate of oil. S/Q or S/W are quite akin to volume hourly or weight hourly space times. Figure 7 shows that for removing sulfur from the Raw Anthracene Oil, essentially same amount of surface areas of the two catalysts would be required. However, with regard to removing nitrogen, surface areas required of two catalysts would be different. This indicates that as far as the desulfurization of lighter stock such as Raw Anthracene Oil is concerned, the unit surface activity of the two catalysts is the same. But the surface activity towards denitrogenation is higher for the Monolith catalyst than for the Nalcomo 474 catalyst.

Figure 8 shows the comparison of the surface activities of the two catalysts on the heavier feedstock, i.e., Synthoil. In this case, the activity of the Monolith catalyst is far greater than that of the Nalcomo 474 catalyst. This behavior is different from that observed on the Raw Anthracene Oil, and as further discussion will show, this difference in the superiorities of the Monolith catalyst on the two feedstocks throws light on some interesting and important observations and conclusions of this study.

To have a quantitative idea of the higher unit surface area activity of the Monolith catalyst, rate constants based on surface area were considered essential to know. To accomplish this, the global reaction kinetics of desulfurization and denitrogenation were determined. For the desulfurization, the following three kinetic models, as suggested in literature, were tested to see as to which one best represented the data of this study.

$$(1) \text{ Second order; } \frac{1}{C_A} = kt + \frac{1}{C_{AO}}$$

- (2) Combination of two first order reactions; one for the lighter and the other for the heavier fractions of the stock;

$$\frac{C_A}{C_{AO}} = \alpha e^{-k_1 t} + (1 - \alpha) e^{-k_2 t}$$

where α is the fraction of light or heavy component in the feed.

$$(3) \text{ First order; } \frac{C_A}{C_{AO}} = e^{-kt}$$

The second model was discarded because the value of the rate constant k_2 found by the non-linear regression of data was approximately zero which was not considered reasonable on a physical basis. Of the other two models, the first model, i.e., the

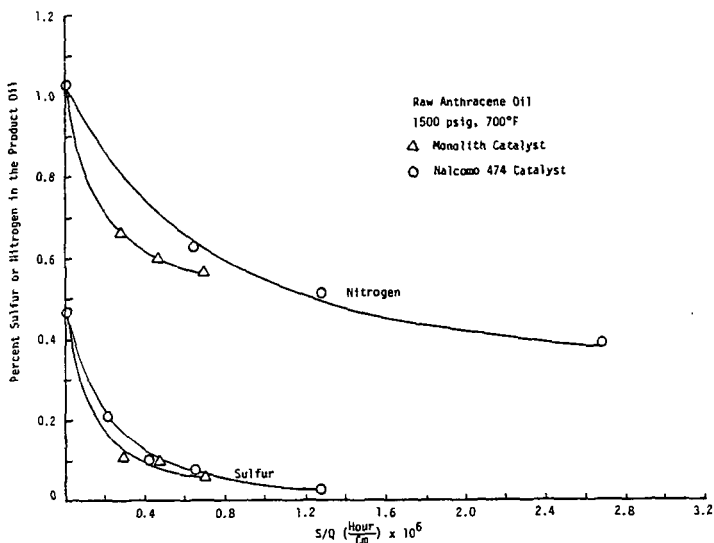


Figure 7: HDS and HDN Responses to the Change in Surface Area/Volumetric Flow Rate of Oil

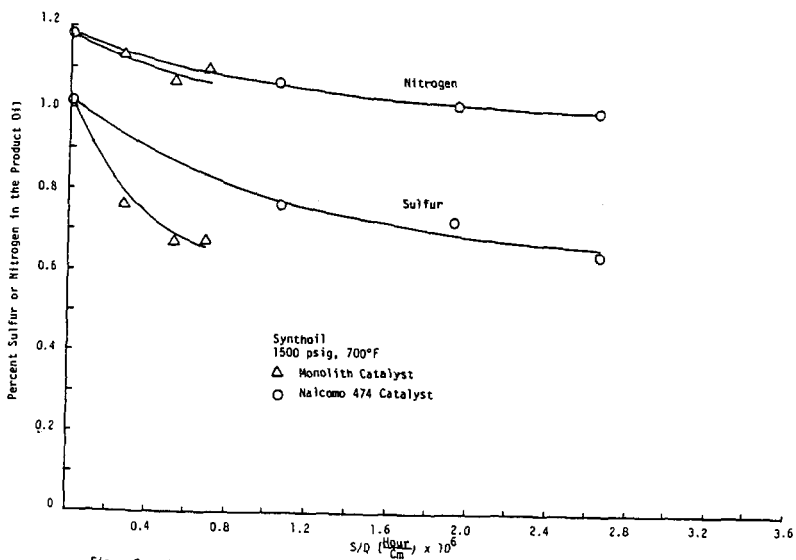


Figure 8: HDS and HDN Responses to the Change in Surface Area/Volumetric Flow Rate of Oil

TABLE V
SECOND ORDER RATE CONSTANTS (VOLUMETRIC)

$$k, \frac{\text{cm}^3}{(\text{gm.})(\text{hour})}$$

	Raw Anthracene Oil		Synthoil	
	Monolith Catalyst	Nalcomo 474 Catalyst	Monolith Catalyst	Nalcomo 474 Catalyst
Desulfurization	8.68	48.8 ^a	0.427	0.431
Denitrogenation	0.724	1.4 ^b	0.084	0.134

TABLE VI
SURFACE AREA RATE CONSTANTS

$$k, \frac{\text{cm}^4}{(\text{gm.})(\text{hour})}$$

	Raw Anthracene Oil		Synthoil	
	Monolith Catalyst	Nalcomo 474 Catalyst	Monolith Catalyst	Nalcomo 474 Catalyst
Desulfurization	2282	2400 ^a	108	25
Denitrogenation	190	81 ^b	24	8.5

^aCorresponds to the volumetric rate constant obtained using Sooter's data (2)

^bCorresponds to the volumetric rate constant obtained using Stachell's data (3)

second order rate expression was found to fit the data better. For denitrogenation, only the first and second order models were examined, and in this case also the latter model was found to represent the data better.

Table V gives the values of the second order rate constants for the HDS and HDN for both liquids and catalysts studied. The values of the rate constants for HDS and HDN of Raw Anthracene Oil using Nalcomo 474 catalyst were obtained by applying the same non-linear regression analysis technique to the data of Sooter (2) and Satchell (3). The comparison of the rate constants lead one to the same conclusion as shown by Figures 5 and 6.

The rate constant based on surface area, k_s , was calculated from the volumetric rate constants by using the following equation:

$$k_s = k \frac{V_r}{S}$$

where k = volumetric rate constant, $\frac{\text{cm}^3}{(\text{hour})(\text{gm.})}$

V_r = volume of the reactor, cm^3

S = total surface area of the catalyst, cm^2

The values of k_s calculated for the various values of k are given in Table VI. In the case of Synthoil, the observed surface area rate constants for desulfurization as well as denitrogenation are about 3 to 4 times higher for the Monolith catalyst than those for the Nalcom 474 catalyst. This further confirms that the observed surface activity of the Monolith catalyst for treating heavier liquids is much higher than the commercial Nalcom 474 catalyst. However, in the case of Raw Anthracene Oil, the observed surface area rate constants for desulfurization are about the same for both catalysts and hence they have the same observed surface activity for this lighter feedstock. But the denitrogenation rate constant even on this liquid is higher for the Monolith catalyst than for the Nalcom 474 catalyst.

Thus, the Monolith catalyst seems to have potential superiority over the commercial catalysts used in this study, especially for treating high boiling stocks.

Reasons for the Higher Observed Unit Surface Area Activity of the Monolith Catalysts:

There can be three main reasons:

- (1) Intrinsic activity of the Monolith catalyst was higher than that of the Nalcom 474 catalyst.
- (2) Fluid dynamic effects in the reactor when Nalcom 474 catalyst was used did not provide efficient solid-liquid contacting.
- (3) There were severe diffusional limitations in the case of Nalcom 474 catalyst, which had a pore radius of 33°A , due to which its surface area utilization was very low as compared to surface area utilization in the case of Monolith catalyst which had pore radius of 80°A .

If one considers that the Monolith catalyst was intrinsically more active than the Nalcom 474 catalyst then the observed superiority of the Monolith catalyst should be almost the same, or at least have the same order of magnitude, when tested on two different feeds. But as explained earlier, the observed surface activities of the two catalysts for HDS are almost equal in the case of Raw Anthracene Oil, while on Synthoil the observed surface activity of the Monolith is about 4 times that of the Nalcom 474 catalyst. Therefore, there is sufficient ground to believe that the Monolith catalyst used in this study was not intrinsically more active than the Nalcom 474 catalyst as far as the HDS was concerned.

In previous studies, Sooter (2) and Satchell (3) observed that reducing the particle size of the Nalcom 474 catalyst from 8-10 mesh to 40-48 mesh did not have any significant effect on the desulfurization and denitrogenation of Raw Anthracene Oil under similar experimental conditions as employed in this study. This suggests that the fluid distribution and hence the fluid dynamic effects were not important in the trickle bed reactors as operated for this work. If these effects were important,

then the reduction in particle size should increase conversion, or the HDS and HDN, by improving fluid distribution and reducing the intraparticle diffusion resistances.

Under the likelihood that the first two reasons do not explain the results of this study or are not important in the present context, intraparticle diffusion limitations appear to be responsible for differentiating the activities of the two catalysts. Tables I and II show that the Synthoil is a high boiling liquid as compared to Raw Anthracene Oil. This means that the molecules that constitute Synthoil are larger on the average than the molecules that constitute the Raw Anthracene Oil. Therefore, the smaller pore size, 330A, of the Nalco 474 catalyst and its longer diffusion path, which is the radius of the catalyst particle, about 1 mm, would offer much higher intraparticle diffusion resistance to Synthoil molecules than to the Raw Anthracene Oil molecules. This would severely limit surface area utilization of Nalco 474 on Synthoil liquid but not as much on Raw Anthracene Oil. Therefore, observed unit surface area activity of Nalco 474 catalyst on Synthoil would be lowered appreciably as compared to the lowering of the activity of the same catalyst on Raw Anthracene Oil. On the other hand, pores of the Monolith catalyst are approximately two and a half times larger than the pores of the Nalco 474 catalyst. The diffusion path is only 0.114 mm, i.e., half the thickness of the channel wall. This is 1/9 times the diffusion path length of the Nalco 474 catalyst. Due to this, the Monolith catalyst would offer much less diffusion resistance to Synthoil molecules than that offered by Nalco 474 catalyst. Therefore, the percent surface area utilization of the Monolith catalyst would be much higher than the percent surface area utilization of the Nalco 474 catalyst. But the larger pore size and smaller diffusion length of the Monolith catalyst could not have any advantage when a lighter feedstock like Raw Anthracene Oil is processed because, as determined by Sooter (2) and Satchell (3), this feedstock does not have significant diffusion problems with the Nalco 474 catalyst.

To have a quantitative idea of the problem of intraparticle diffusion, "Effectiveness Factors" for the two catalysts were calculated from the observed reaction rates using the relationship between η and $\eta(5)$ and the "triangle method" suggested by Satterfield (4). The Effectiveness Factors for the Monolith and Nalco 474 catalyst were found to be 0.94 and 0.216, respectively.

SUMMARY

The results of this study indicated that at the reactor operating conditions of 371 C and 1500 psig, the observed HDS activity based on unit surface area, was much higher for the Monolith catalyst as compared to the Nalco 474 catalyst when processing the heavier feedstock, i.e., Synthoil. But it was about the same when processing a lighter feedstock like Raw Anthracene Oil. Since the average pore radius and the intraparticle diffusion length of the Monolith catalyst were 87.6 μ A and 0.114 mm against 31 μ A and 1 mm of the Nalco 474 catalyst, the intraparticle diffusion was considered to be responsible for the lower observed activity of the Nalco 474 catalyst on the heavier feedstock. From the observed rates of reaction, the Effectiveness Factors for the Monolith and Nalco 474 catalysts were found to be 0.94 and 0.216, respectively, for the HDS of Synthoil.

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